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AUTHOR: Chang, Hua (1728/5478)

TITLE: Energy band theory and the migration of excitation energy in protein molecules

PERIODICAL: Hua Hsüeh Hsüeh Pao, v. 28, no. 3, 1962, 132-138

TEXT: The theories of Szent-Gyorgyi and Schmitt and Even's calculations on the structure of proteins are either incomplete or are contradicted by experimental data. The author investigated the π-electronic structure of peptide bonds using the LCMO process and derived the energy band theory for polypeptides. Based on the protein structure theory developed by Pauling and Milliken, polypeptide molecules are considered composed of many sections and taking into account the effect of hydrogen, the author determined that monomer CO-NH has 4 π-electrons distributed on the carbonyl and amino radicals. The carbonyl radical is the electron recipient and the amino radical is the electron donor. When the radicals are put together electrons migrate from the donating radical to the receiving radical. The π-electronic systems

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of CO-NH monomers are of three structural types: (1) Basic type — two electrons in each of the amino radicals and the carbonyl radical and the monomer is in the non-excited status. (2) Charge migration type — one π-electron of amino radical migrates to the energy level of the carbonyl radical. (3) Localized excitation type — one π-electron of carbonyl radical migrates from the radical status to the excited status. The types may be expressed in wave functions Ω_1, Ω_2, and Ω_3 as

$$\Omega_1 = \frac{1}{\sqrt{4!}} \sum_P (-1)^P P \left\{ \varphi_1(1)\alpha(1)\varphi_1(2)\beta(2) \chi_N(3)\alpha(3)\chi_N(4)\beta(4) \right\}$$

$$\Omega_2 = \frac{1}{\sqrt{4!}} \sum_P (-1)^P P \left\{ \varphi_1(1)\alpha(1)\varphi_1(2)\beta(2) \psi_3(3)\alpha(3)\chi_N(4)\beta(4) \right\}$$

$$\Omega_3 = \frac{1}{\sqrt{4!}} \sum_P (-1)^P P \left\{ \varphi_1(1)\alpha(1)\varphi_2(2)\beta(2) \chi_N(3)\alpha(3)\chi_N(4)\beta(4) \right\}$$

where p is the substituting symbol; α, β are self-spinning wave functions; χ_N, the π-

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electron orbits of amino radical and ψ_1 and ψ_2 are π-electron orbits of cis- and trans- carbonyl bonds respectively. According to Kon,

$$\psi_1 = 0.5472 \, X_c + 0.8370 \, X_0$$
$$\psi_2 = 0.8370 \, X_c - 0.5472 \, X_0$$

where X_c and X_0 are the $2P\pi$ atom orbits of carbon and oxygen respectively. The linear equation group obtained from Schrodinger's equation is

$$(H_{11} - E)C_1 + H_{12}C_2 + H_{13}C_3 = 0$$
$$H_{21}C_1 + (H_{22} - E)C_2 + H_{23}C_3 = 0$$
$$H_{31}C_1 + H_{32}C_2 + (H_{33} - E)C_3 = 0$$

where

$$H_{ii} = \int \Omega_i H \Omega_i \, d\tau$$
$$H_{ij} = H_{ji} = \int \Omega_j H \Omega_i \, d\tau$$

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H is the Hamilton symbol for the CO-NH 4π-electron system. The equation group may be in the form of

$$H_{22} = I - A - (0.5472)^2 \int X_C^2(1) \left(\frac{e^2}{r_{12}}\right) X_N^2(2) \, d\tau_1 d\tau_2 -$$

$$- (0.8370)^2 \int X_O^2(1) \left(\frac{e^2}{r_{12}}\right) X_N^2(2) \, d\tau_1 d\tau_2$$

$$H_{12} = 0.8370\sqrt{2}\,\beta_{CN}$$

$$H_{23} = -0.5472\,\beta_{CN}$$

$$H_{13} = 0$$

where I is the ionization energy of the amino radical; A, the electronic attraction potential; β_{CN}, the integral of $\int X_C H X_N d\tau$. The structural wave functions Ω_1 and Ω_2 can be expressed by the following structural formulas respectively:

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As to the status of π-electron system in peptide bond CO-NH $(\cdots CO\text{-}NH\cdots)_{N-2}$ CO - NH, the above-mentioned status wave functions and corresponding energy levels satisfy equation $H\psi_i = E_i \psi_i$, $i = 1, 2, 3$

when N peptide monomers close up and form N polymers with (N-1) H bonds, the π-electron molecular orbit will change in form and the potential energy of the monomers will increase from U_n to V

$$V = \sum_{n=1}^{N} U_n$$

the width of energy band obeys approximately equation

$$\left(-\frac{\hbar^2}{2m}\Delta + U\right)\phi_o = E\phi_o$$

In the N polymers, the wave function of π-electron status must satisfy Schrödinger's equation

$$\mathscr{H}\phi = \mathscr{E}\phi$$

where $\mathscr{H} = \left(-\frac{\hbar^2}{2m}\Delta + V\right)$

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The linear combination for individual wave function of N monomers in the single peptide potential field is

$$\phi = \sum_{n=1}^{N} A_n \phi_o^{(n)}$$ or

$$\sum_{n=1}^{N} (\mathscr{H}_{mn} - \mathscr{S}_{mn}\mathscr{E})A_n = 0$$ $m = 1, 2, \ldots N$

where $\mathscr{H}_{mn} = \int \phi_o^{(m)} \mathscr{H} \phi_o^{(n)} \, d\tau$

$$\mathscr{S}_{mn} = \int \phi_o^{(m)} \phi_o^{(n)} \, d\tau$$

For the same peptide monomers, $\mathscr{H}_{mn}$ and $\mathscr{S}_{mn}$ relate to the distance between monomers. The necessary condition for the linear equations with solutions of other than zero, is

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$$\begin{vmatrix} E - \mathcal{E} & \beta & 0 & \cdots & 0 & 0 & 0 & 0 \\ \beta & E - \mathcal{E} & \beta & \cdots & 0 & 0 & 0 & 0 \\ 0 & \beta & E - \mathcal{E} & \cdots & 0 & 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \ddots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & E - \mathcal{E} & & \beta & \\ 0 & 0 & 0 & \cdots & \beta & & E - \mathcal{E} \end{vmatrix}_N = 0$$

From this, we obtain energy levels

$$\mathcal{E}_m = E + 2\beta \cos \frac{m\pi}{N+1} \qquad m = 1, 2, \ldots N$$

when N is large, continuous energy bands will occur, width of the band will be 4β. The difference between the the highest energy level and the lowest one is

$$W_g = E_2 - E_1 - 4 |\beta|$$

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Take Evan's β value, the experimental value for $E_2 - E_1 = 6.1$, 0.3 from the theoretical value of 6.4. It is concluded that there are common points between cyclically and repeatedly structured polypeptides and crystals. When N monomers transit from isolated status to a regular integral body the energy levels of the monomers will split into continuous energy bands whose density is in proportion to N and whose width is in proportion to the intensity of interaction. In protein molecules the intensity is rather low, therefore the energy band is narrow (0.8ev.) while the width of the counter band is large (5.3 ev.). Thus proteins are insulators under nonexcited status. However when excited, their π-electrons migrate along the hydrogen-peptide bond and form an electronic vacancy in the band and the energy of the bands is released in the form of photo-waves (fluorescence). In regularly structured protein molecules excited electrons can migrate anywhere. In the case that the order of hydrogen bonds is destroyed the common π-electron collecting energy level will not exist nor will any nonlocalized π-electron. The regularly structured protein molecules linked by hydrogen-peptide bonds may allow the migration of excited energy. The theoretical

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value for the migration obtained by the author is 5.3 ev. The numerous hydrogen bonds in and among protein molecules forms the hydrogen-peptide lattice structure and the locally excited monomers enable the excited energy to migrate within the entire molecular system. Further research on the theory of the change of protein structure and the molecular vacancy caused from changes in external conditions is recommended. The author thanks Hsü.Kuang-hsien (1776/0342/2009) for assistance. There is 1 figure. References in English include: A. Szent-Gyorgyi, Science 93, 609 (1941); S. Nagakara, Molecular Phys. 3, 105 (1960); K. Watanabe, J. Chem. Phys. 26, 542 (1957).

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